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The Role of Pu_2O_3 and Defects in The PuO_2 Layer in The Plutonium Hydriding Process

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INTRODUCTION

Experiments were conducted to verify that Pu_2O_3 catalyzes hydriding and to demonstrate that hydriding is promoted by direct exposure of Pu_2O_3 to H_2, defects and inclusions in the PuO_2 layer covering Pu. An alternative to the hydrogen diffusion through PuO_2 mechanism for nucleation of hydriding [1] is then proposed for cases in which the dioxide is not ideal and/or the hydrogen solubility in the metal exceeds that of PuO_2.

EXPERIMENTS

All experiments were done with Pu samples with ~ 10 ppm hydrogen impurity. The Pu samples were mounted in indium o-ring sealed aluminum sample holders to seal the samples' edges and back sides from any subsequent reactive gas exposure. No scratch was created on the surfaces of samples 1, 2, and 3, but a small deep scratch was intentionally created near the center of samples 4, 5, and 6. Each of these samples was then placed inside a separate reaction chamber and pumped at room temperature to a base pressure of 10^{-2} Pa. Samples 7, 8, and 9 were simultaneously pumped and heated to 110°C for ~ 2 days to convert some portion of the dioxide outer layer into Pu_2O_3 [2-3] then cooled down to room temperature in vacuum. At the end of the pumping stage, each reaction chamber was quickly filled with 0.007 moles of H_2 to allow for fast and expanded measurement of rates. All reactions were performed with research grade hydrogen. Pressure was measured with quartz oscillator gauges. Images/movies of the hydriding reactions were also recorded.

RESULTS

The induction time for samples 1-3 was ~ 100 seconds while their reaction time was approximately 700-850 seconds. The variation in the total reaction time among these three samples was due to the difference in the nucleation spots on the each sample. Samples 4-9 exhibited almost no induction time and had a reaction time of 540-700 seconds. Samples 4-6 had a deep scratch near the center of each sample. The deep scratch exposed the Pu_2O_3 layer below the

PuO_2 to direct contact with H_2. The deep intentional scratches on samples 4-6 were always observed to be among the first nucleation sites for hydriding. The ejection of hydride powder from the main hydriding spots to surrounding area to start new satellite hydriding spots and the initial number of initiation sites were very much unpredictable, and the time to complete reaction varied among these scratched samples. The time to complete reaction for samples 7-9 varied due to the difference in exposed local Pu_2O_3 areas on each sample at the time of exposure to hydrogen. But even so, there was fair overlap in the reaction time for samples with exposed Pu_2O_3 areas. The exposed Pu_2O_3 catalyzes H_2 into atomic hydrogen and transports the radicals quickly to the Pu interface for hydriding reaction [2-3].

Camera images revealed the existence of 3 or 4 small unknown dark spots near the bottom edge of sample 2 before H_2 exposure. These dark spots might be defective oxide, impurity inclusions, or surface abnormalities of some sorts. They were among the first sites to nucleate. By 30% reaction, they were among the largest hydriding spots. For samples with the intentionally scratched spots (exposed Pu_2O_3), the scratched areas also developed into the largest growing hydring sites at around 30% reaction. On the contrary, multiple nucleation sites sprang up all over the surface of samples 7 to 9. At 30% reaction, the surface of these samples already exhibited nearly uniform surface corrosion. This mode of corrosion is consistent with hydriding attack on a Pu surface covered mostly with Pu_2O_3. Hydrogen solubilities in actinide oxides are many orders of magnitude less than that in pure metals [4, 5]. The 10ppm hydrogen impurity of the Pu samples under investigation is at least 100-1000 times the solubility of hydrogen in PuO_2. So, as PuO_2 formed during machining and exposure to oxide species, the hydrogen in excess of the maximum solubility of hydrogen in PuO_2 had to diffuse toward the Pu/oxide interface. The PuO_2 layer on these Pu samples was already saturated with hydrogen and would act as a barrier for any hydrogen diffusion through it. Any hydrogen diffusion through the PuO_2 layer must have been through defects in the oxide layer such as oxygen vacancies, micro-cracks, structural defects, or plutonium impurity

inclusions such as plutonium oxy-carbide and some other unwanted impurities introduced into the oxide layer during machining. Once a local hydriding spot in the dioxide layer pops up, it can release heat and reduces the local dioxide to Pu_2O_3 promoting further corrosion.

SUMMARY

Experiments were performed to demonstrate the catalytic role of Pu_2O_3 in hydriding corrosion. Defects and inclusions in the PuO_2 layer also seem to serve as conduits for hydriding. An alternative to the hydrogen diffusion through PuO_2 mechanism for nucleation of hydriding is proposed for cases in which the dioxide is not ideal and/or the hydrogen solubility in the metal exceeds that of PuO_2.

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